



Project Summary

A Comparative Evaluation of Two Extraction Procedures: The TCLP and the EP

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The 1984 amendments to the Resource Conservation and Recovery Act (RCRA) require that the U.S. Environmental Protection Agency (EPA) restrict the land disposal of hazardous wastes. The Extraction Procedure Toxicity Characteristic (EP) test is used to determine if an improperly managed waste poses an unacceptable risk to groundwater and should therefore be managed as a hazardous waste. Regulatory thresholds, based on the EP test, have been established for eight metals, four pesticides, and two herbicides.

The Toxicity Characteristic Leaching Procedure (TCLP) is a newer regulatory test developed to address a Congressional mandate to identify additional characteristics of wastes, primarily organic constituents, that may pose a threat to the environment. The TCLP has been promulgated for use in determining specific treatment standards associated with the land disposal restrictions of RCRA. The TCLP has also been proposed as a replacement procedure for the EP test.

Two studies were conducted to compare the results of the TCLP with those of the EP. In the first study, a synthetic heavy metal waste was chemically solidified/stabilized with and without a variety of interfering compounds. The solidified/stabilized waste was cured for 28 days and subjected to the TCLP and EP extractions. The extracts were analyzed for Cd, Cr, Ni, and Hg. In the second study, two solidified/stabilized, heavy metal wastes and an untreated perchloroethene (PCE) still-bottom waste were used. Twelve volatile organic compounds were added to each waste type at two ratios. The EP and TCLP were

performed on three samples from each waste type. The extract from each sample was analyzed for As, Ag, Ba, Cd, Cu, Ni, Pb, and Zn and for the 12 volatile organic compounds. The losses due to the mechanics of the TCLP and EP extractions were also estimated by spiking the TCLP and EP extracts with known concentrations of organic compounds before and after extracting the wastes.

The results of these studies indicate that, for most of the metal contaminants, the TCLP and EP produce similar results when TCLP extraction fluid 2 (acetic acid solution) is used but differ when TCLP extraction fluid 1 (acetate buffer) is used. The results of testing for volatile organic contaminants indicate that, for 8 of the 12 contaminants, the concentrations measured in the TCLP extractants were significantly greater than those measured in the EP extractants.

This Project Summary was developed by EPA's Risk Reduction Engineering Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

One of the most significant dangers posed by hazardous waste stems from the leaching of toxic constituents into groundwater. The EPA EP test addresses the properties of a waste that are directly related to the potential of the waste to pose a hazard to groundwater when disposed of in a landfill environment. The toxicity characteristic is assessed when the waste is subjected to the EP, and the extract is analyzed for



eight metals, four pesticides, and two herbicides.

The TCLP is a "second-generation" extraction procedure developed by the EPA. The TCLP is proposed as a replacement for the EP test as a waste characterization pool. This procedure has also been proposed as a method of addressing the shortcomings of the EP. Since the TCLP was first published in the *Federal Register* in 1986, it has undergone several modifications. This study was conducted using the June 13, 1986, publication of the TCLP. More recently, the November 7, 1986, version of the TCLP method has been published in the Code of Federal Regulations, Part 267, Appendix I.

There are many differences between the EP and TCLP methods, some of which are obvious; others are buried within the procedures. The most obvious difference is that the TCLP requires the use of the zero-headspace extraction (ZHE) vessel for volatile compounds and an extraction fluid selection step for nonvolatile extractions. Other differences include:

- In the TCLP method for nonvolatiles, one of two extraction fluids is selected to extract the solid waste sample. The type of extraction fluid is determined in an initial test on the waste and is based on the waste's alkalinity. Extraction fluid 1 is an acetate buffer at a pH of 4.93 ± 0.05 . Extraction fluid 2 is an acetic acid solution with a pH of 2.88 ± 0.05 . The EP uses distilled deionized water as an extraction fluid, and 0.5 N acetic acid is added to the solid waste/water slurry to maintain the pH at 5.0 ± 0.2 . The acetic acid is added as required, up to a maximum of 4 g of 0.5 N acetic acid per 1 g of solid waste.
- The TCLP method for volatiles requires the use of extraction fluid 1. The EP has no volatiles extraction procedure.
- The TCLP requires that the ZHE vessel be used for volatiles extraction.
- The TCLP procedure requires the use of 0.6- to 0.8- μm glass fiber filter and excludes the use of prefilters. The EP requires the use of 0.45- μm cellulose triacetate filters and allows the use of glass fiber prefilters.
- The TCLP requires that the particle size of the solid be small enough to pass a 9.5-mm standard sieve. The EP allows the use of the Structural Integrity Procedure if the sample is monolithic in nature. If the sample is not a monolith, the EP requires that the particle size be small enough to pass a 9.5-mm standard sieve.

- The TCLP requires rotary agitations in an end-over-end fashion at 30 ± 2 rpm. The EP allows the use of either a stirred open vessel or a rotary end-over-end agitator.
- The extraction period for the TCLP is 18 hr. The extraction period for the EP is 24 ± 2 hr.
- The EP requires monitoring and adjustment of the pH during the extraction. The TCLP does not.

This study was designed to compare the extraction efficiencies of the TCLP with those of the EP. This comparison was accomplished in two ways. In the first, the metal-extraction effectiveness of the two extraction methods was evaluated on a synthetic metal sludge, with and without different interfering materials. The second involved evaluating the efficiency of the extraction of selected volatile compounds from three solidified/stabilized wastes and evaluating the loss of the volatiles during both the process of conducting the extractions and the storage of the extracts before their analyses.

Procedures

In the first study (A), a synthetic metal sludge containing cadmium (Cd), chromium (Cr), nickel (Ni), and mercury (Hg) was treated with a lime/kiln dust binding agent. During the mixing process, three concentrations of 10 materials that might interfere with the binding and contaminant containment properties were added to the sludge. A different batch of waste/binder was mixed for each of the interfering materials. After the materials had cured under constant temperature and 100% humidity for at least 28 days, samples were ground and subjected to the EP and TCLP tests.

In the second study (B), two of the wastes, the metal plating sludge and metal plating solution, were first solidified using Type 1 Portland cement as binding agent. Separate batches of the two solidified wastes and perchloroethene (K030) still-bottom waste were divided into two portions, and a solution of 12 volatile organics was added at either 0.1 or 1.0 weight percent. The volatile organics included chloroform, carbon tetrachloride, benzene, toluene, ethylbenzene, two ketones, and five di-, tri-, and tetra-chloromethane and chloroethene compounds. The wastes were cured for 14 days, and samples were subjected to the EP and TCLP tests. The EP and TCLP extracts were analyzed for metals and volatile organic compounds.

A separate part of this study was designed to detect any losses of volatile organics that might occur during the EP and

TCLP procedures or during subsequent extract handling and storage. The leachate solutions were spiked during two separate steps of the EP and TCLP, either before extraction or after the liquid/solid separation step.

Both studies were intended as multifactor factorial experimental designs to facilitate statistical analysis. Complete internal and external laboratory quality assurance/quality control measures were used throughout.

Results and Discussion

Study A - Leaching of the Solidified Metal Sludge

The concentrations of the metals in the solidified sludges that were released in the EP and TCLP extractions in Study A are summarized in Figures 1 through 4. The results were normalized to the total amount of metal extracted to correct for the difference in amount of extractant used in the two tests.

As illustrated in Figure 1, for 34 of the 40 conditions under which the TCLP and EP were compared, the EP extracts contained higher concentrations of cadmium. These results, however, are not statistically significant, perhaps because of the high variability in the data. Nickel concentrations (Figure 2) are similar for both extraction procedures (18 having lower TCLP and 22 lower EP concentrations). Chromium (Figure 3) and mercury (Figure 4) concentrations were higher in the TCLP extracts (25 of 40 chromium and 28 of 40 mercury having higher TCLP extract levels).

All extractions of the metal sludges used extraction fluid 2 for the TCLP and the full amount of acid for the EP so that the buffering capacity of the EP and TCLP extraction fluids was equal. The small but significant differences seen in the amounts of chromium and mercury extracted by the TCLP procedure cannot be attributed solely to pH influences but must be a function of other differences between the extraction procedures such as time of extraction or method of agitation.

Study B - Organic Extraction from Metal Wastes and Still Bottoms

Metals in Extracts

The two solidified/stabilized metal wastes produced TCLP and EP extracts that were not significantly different for the majority of cases studied (Figure 5). Arsenic and lead were the only contaminants for which

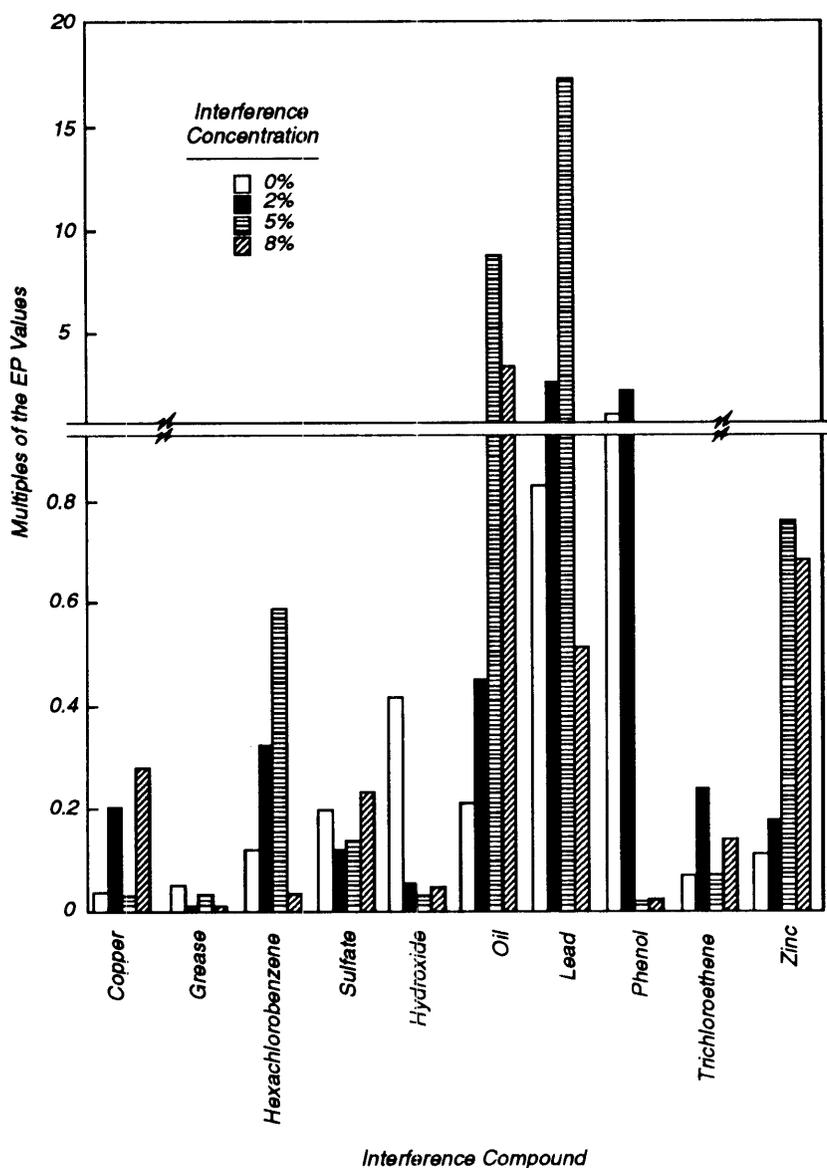


Figure 1. Average normalized Study A cadmium extract concentrations expressed as the TCLP concentration divided by the EP concentration.

the TCLP extracts were significantly more concentrated than were those of the EP. Again, for these solidified wastes, extraction fluid 2 was used, which is identical in alkaline neutralization capacity to the EP extraction fluid when all 400 ml of the acetic acid is required.

Organics in Extracts

With some exceptions, TCLP extracts typically contained about one and a half times as much of each of the organics as did the EP extracts (illustrated for the 1% spiked

sample in Figure 6). Extracts from the 1% spiked samples averaged only about 50% higher organic levels than did those of the 0.1% spiked samples. No correlation was found with any of the physical properties of the organic materials, such as vapor pressure, solubility, pH, or boiling point.

Volatile Losses

The wastes were spiked in different steps of the TCLP and EP procedures to give an indication of the amount of loss of the organics during the test. When chlorobenzene

and carbon disulfide were added to the extraction fluid before leaching, over 99% of both were lost. The organics were either absorbed by the waste solids or were lost from the extracting fluids during the procedure.

Spiking the extraction fluid after the leaching procedure resulted in 5% to 20% loss of chlorobenzene and about 10% to 25% loss of carbon disulfide. Evidently, a maximum of about 25% of the volatile organic spike was lost during sample placement in the sample vial, storage, and analysis. The high recoveries indicate that the materials were probably well dispersed so that the loss of carbon disulfide and chlorobenzene from the samples spiked before leaching cannot be attributed to poor sample dispersion.

Conclusions and Observations

This study was conducted to compare the results of the TCLP and the EP. The EP and TCLP extractions were performed on a number of different wastes subjected to a variety of conditions. Based on the results of this study, the following conclusions were drawn and observations made.

- Generally, the TCLP was a more aggressive leaching procedure than was the EP.
 - When TCLP extraction fluid 2 was used to extract metal contaminants, the EP and TCLP produced similar results.
 - When TCLP extraction fluid 1 was used to extract metal contaminants, the EP and TCLP produced statistically different results, with the TCLP generally being the more aggressive extraction.
 - The TCLP ZHE was only a slightly more aggressive extraction for volatile organics than was the EP extraction in this study.
- Although the TCLP ZHE was a more aggressive extraction procedure than was the EP for the volatile organics, the difference in the concentrations of volatile organics in the TCLP and EP extracts was less than expected.
- When the ZHE vessel was used, cross contamination presented a potential problem.
- The TCLP and EP extraction of the solidified/stabilized specimens appeared to produce conditions that permit dechlorination reactions to occur. Significant amounts of 1,1-dichloroethene were detected in the TCLP and EP extracts although no 1,1-dichloroethene was added, and none was detected in the raw wastes.

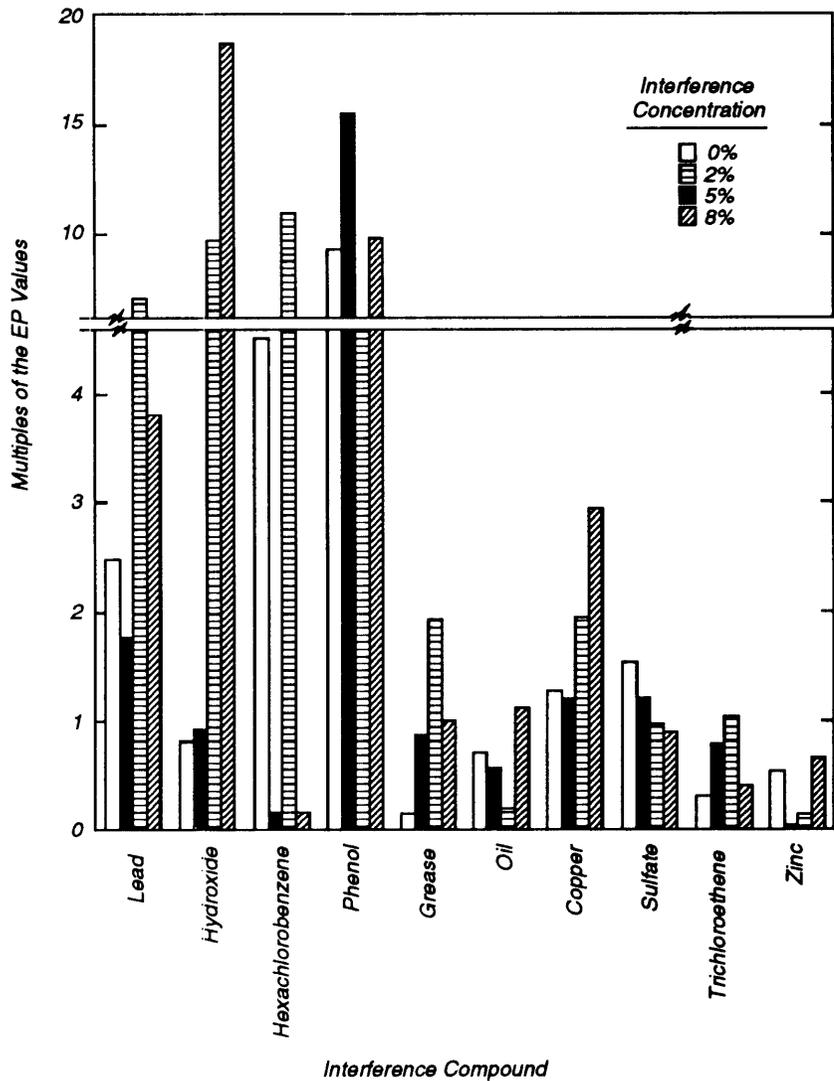


Figure 2. Average normalized Study A nickel concentrations expressed as the TCLP concentration divided by the EP concentration.

Recommendations

The TCLP method, although more difficult to perform than the EP method, is an extraction test that can be performed in most laboratories. The TCLP method, unlike the EP method, addresses semivolatile and volatile contaminants. Several areas should be clarified in the TCLP extraction method. The following recommendations are based on the results of this study.

- (1) The ZHE vessel is difficult to clean. The TCLP method needs to make rec-

ommendations on the most effective method of cleaning the ZHE vessel. Modification of the value design is highly recommended to improve cleaning techniques.

- (2) The TCLP method is vague about procedures for sample collection from the ZHE vessel when Tedlar bags are not used. A section describing the collection of a sample using volatile vials should be included in the TCLP method.

- (3) Additional research should be initiated to investigate why volatile chlorinated compounds extracted from solidified/stabilized wastes are converted to other chlorinated forms.

The full report was submitted in fulfillment of Interagency Agreement No. DW930146-01 by the U.S. Army Engineer Waterways Experiment Station under the sponsorship of the U.S. Environmental Protection Agency.

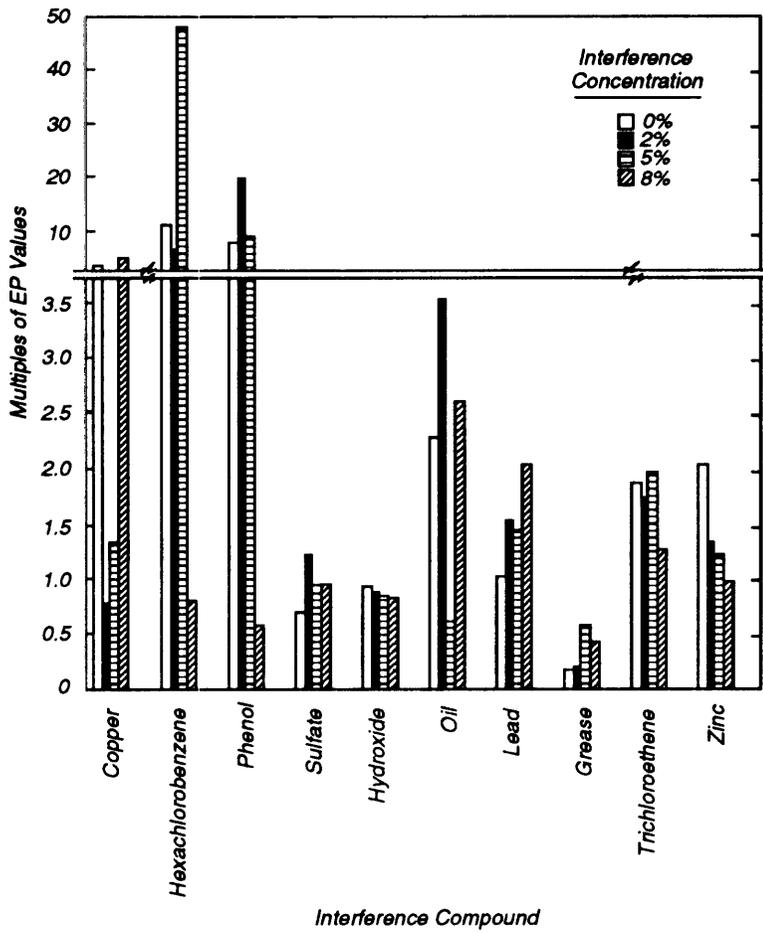


Figure 3. Average normalized Study A chromium extraction concentrations expressed as the TCLP concentration divided by the EP concentration.

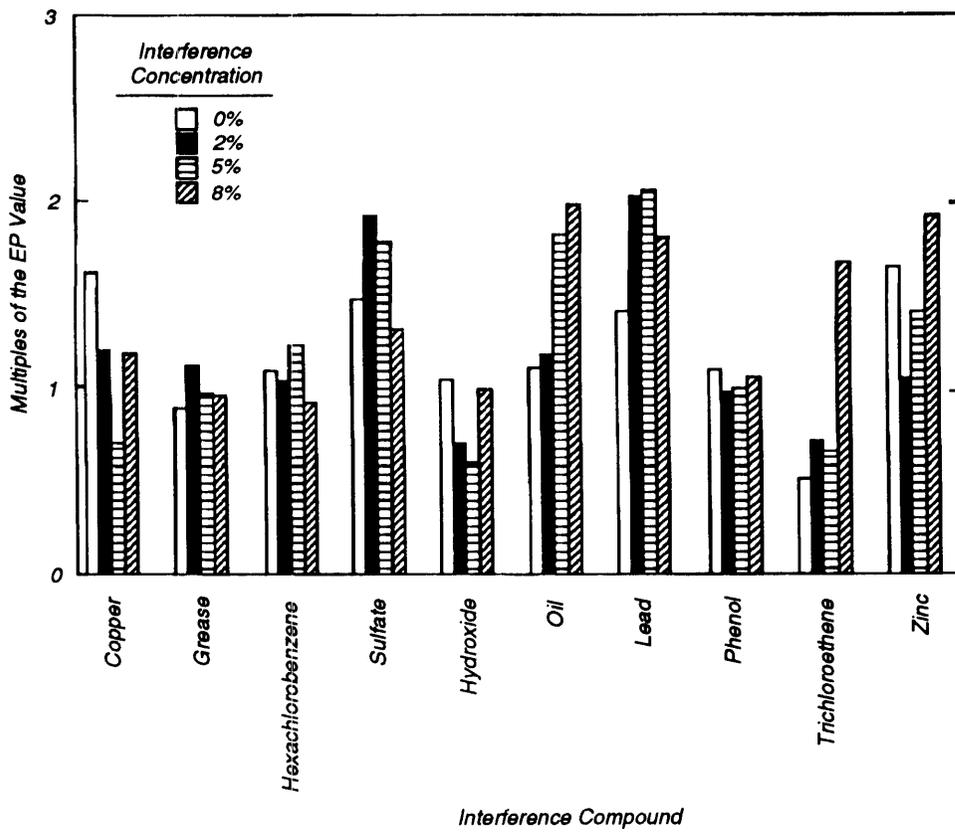


Figure 4. Average normalized Study A mercury extract concentrations expressed as the TCLP concentration divided by the EP concentration.

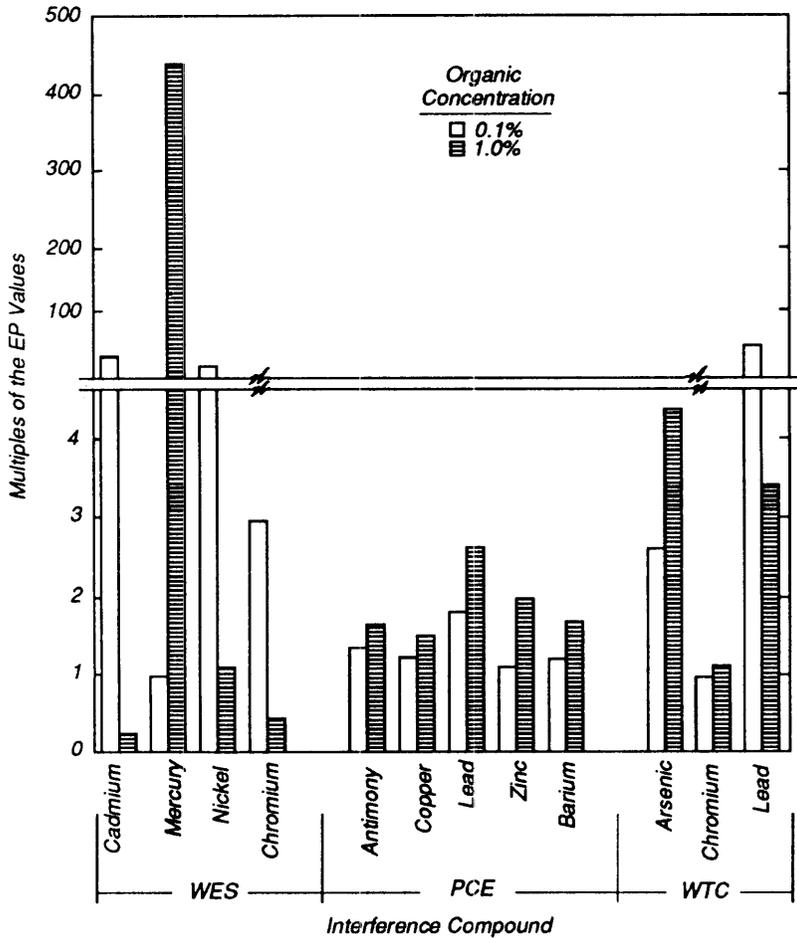


Figure 5. Average normalized Study B metal extract concentrations expressed as the TCLP concentration divided by the EP concentration.

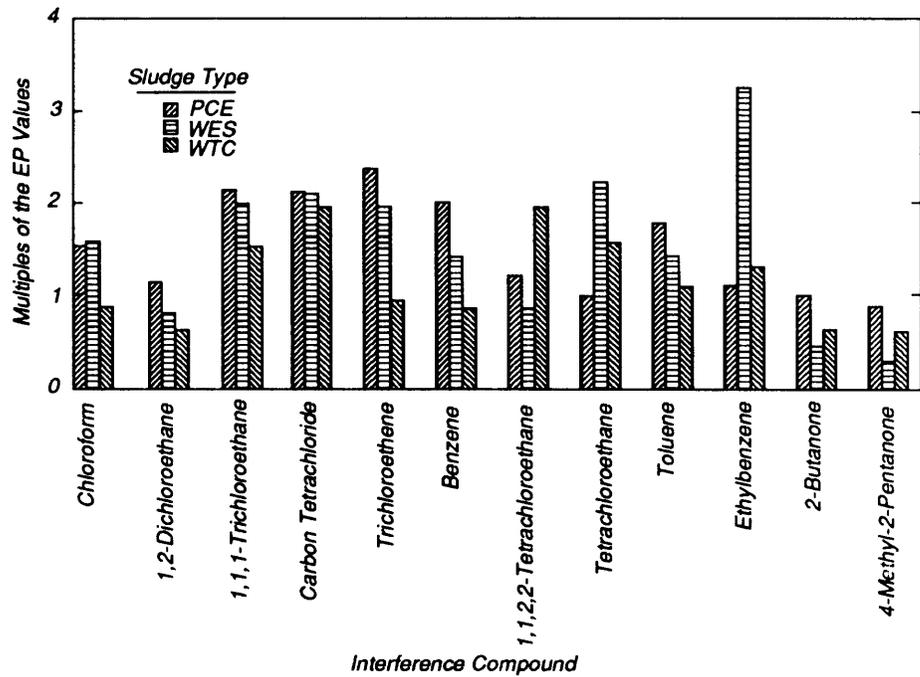


Figure 6. Average normalized Study B 1.0 percent organic extract concentrations expressed as the TCLP concentration divided by the EP concentration.

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Carlton C. Wiles is the EPA Project Officer (see below).

The complete report, entitled "A Comparative Evaluation of Two Extraction Procedures: the TCLP and the EP " (Order No. PB91- 240 564/AS; Cost: \$26.00, subject to change) will be available only from:

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